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(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Modular System and Process for the Production of Aqueous Coating Compositions

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Modular system and process for the production of aqueous coating compositions.

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This invention relates to a modular system (a mixed system composed of modules), which is suitable for the production of various types of aqueous coating compositions. In particular, it is suitable both for the production of 10 aqueous effect base lacquers, single-tone aqueous base lacquers and aqueous single-coat topcoat lacquers with an adjustable colour tone and/or effect, and for the production of aqueous clear lacquers, which may in particular be used in automotive and automotive component 15 lacquer coating.

Water-borne lacquer systems are being used to an ever increasing extent in automotive and automotive component lacquer coating. Especially with regard to aqueous base 20 lacquers, there is, for example, a requirement for a constantly changing number of colour tones and effects, which is rendering economic production and storage increasingly difficult. One way to solve this problem is to provide a limited number of individual, storable components 25 which, depending upon the desired effect or colour tone, may be combined shortly before application to produce the finished, aqueous base lacquer.

EP-A-0 399 427 thus describes a modular aqueous base 30 lacquer system consisting of five components which, once combined, yield a complete aqueous base lacquer. In this process, the effect component, the component with the effect pigments, must be produced and stored without water. This is achieved by solubilising, for example, metal 35 pigments in a solvent-based solution of an alkyd, acrylate or polyester resin and in an organic solvent. The aqueous base lacquers formulated with this effect component thus have an undesirably high solvent content. Moreover, a separate neutralisation component is necessary which

contains ammonia to neutralise the acidic resins in the effect, resin and pigment component.

EP-A-0 468 293 and EP-A-0 471 972 also describe aqueous 5 lacquers based on various components. It is, however, necessary for the effect component to be anhydrous. The resins contained in the effect component and pigment component are anionically or optionally non-ionically modified. In these cases too, a neutralising component 10 containing ammonia is provided.

DE-A-4 110 520 describes a mixed system which is intended to be suitable for the production of aqueous pigmented coating compositions with precisely adjusted colour 15 shading. In particular, aqueous base lacquers are to be produced using this method. The mixed system consists of various pigmented base coatings (A), which contain less than 5 wt.% of water, are preferably anhydrous and contain pigments, solvents and water-dilutable binders, and a 20 pigment-free component (B) containing water, which in particular contains water-dilutable binders and/or rheological additives. The water-dilutable binders contained in component A) are present in organic solvents. The aqueous base lacquers formulated in this manner thus 25 have an undesirably high solvent content. The complete coating compositions are produced by mixing the components directly before application, they are not stable in storage.

30 The as yet unpublished German applications P 4 307 498 and P 4 301 991 from this applicant describe modular systems (mixed systems) for the production of aqueous single-tone and effect base lacquers, which each consist of a binder module and a colour and/or effect module. Both the binder 35 module and the colour and effect module contain anionically and/or non-ionically stabilised water-dilutable resins.

The object of the present invention is to provide a modular system (mixed system) which, starting from a standard binder module, may be used for the production of various aqueous coating compositions, such as base lacquers, 5 single-coat topcoat lacquers and/or clear lacquers, by means of an appropriate combination of the individual modular components. In this system, both the individual modular components and the coating compositions which may be produced therefrom are intended to be stable in storage 10 for an extended period and to have a low solvent content. The individual modular components of the system are intended to be simply miscible with each other in order to produce the particular desired coating composition.

15 It has been found that this object may be achieved by the provision of an aqueous modular system on the basis of cationically stabilised resins. The modular system consists of at least two modular components, wherein one of the modular components is in each case a binder module and the 20 second modular component is selected from among a colour module, an effect module, a crosslinking module and/or a rheological module depending upon the use of the coating composition produced with the modular system or as a function of the desired achievable effect.

25 The present invention accordingly provides a modular system for the production of aqueous coating compositions, containing

30 A) at least one aqueous binder module containing one or more cationically stabilised water-dilutable (meth)acrylic copolymers and one or more cationically stabilised water-dilutable polyurethane resins and/or one or more cationically stabilised water-dilutable 35 (meth)acrylated polyurethane resins, optionally combined with non-ionically stabilised water-dilutable binders, water, optionally together with one or more

organic solvents and/or conventional lacquer additives,

together with at least one of the following modules:

5 B) one or more colour modules containing water, one or more coloured pigments and/or extenders and one or more cationically stabilised polyurethane paste resins, at least 6 wt.% of water, optionally together with one or more water-dilutable cationically and 10 optionally non-ionically stabilised binders, one or more organic solvents and/or conventional lacquer additives,
and/or

15 C) one or more effect modules containing water, one or more effect pigments, at least 6 wt.% of water, one or more cationically stabilised water-dilutable (meth)acrylated polyurethane resins, which may optionally be present combined with further 20 cationically or non-ionically stabilised water-dilutable binders, optionally together with one or more organic solvents and/or conventional lacquer additives
and/or

25 D) one or more crosslinking modules containing one or more crosslinking agents, optionally together with one or more organic solvents, water and/or conventional lacquer additives,
30 and/or

35 E) one or more rheological modules containing one or more organic and/or inorganic rheological control agents, optionally together with one or more cationically, or cationically and non-ionically and/or non-ionically stabilised water-dilutable binders and/or one or more organic solvents and/or water.

Modules are here taken to be storage-stable components from which a complete coating composition may be produced by mixing, which composition may optionally still be adjusted to application viscosity.

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It has been found that it is possible, by mixing the individual modules prepared according to the invention, to prepare various aqueous coating compositions, such as for example aqueous effect base lacquers, single-tone base lacquers, single-coat topcoat lacquers and clear lacquers, without needing to make use of different starting materials. This results in the advantage that coating compositions for different intended applications may be produced starting from standard components. This may be achieved by appropriate selection of the modular components defined within the modular system according to the invention; it is also possible to obtain desired adjustable colour tones and/or effects by mixing the individual modules.

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It has been found that stable modules and complete systems may be obtained according to the invention if the colour and effect modules contain at least 6 wt.%, preferably at least 10 wt.%, of water.

25

Single-coat topcoat lacquers which may be produced from the modular system according to the invention should here be taken to be those coating compositions which form the final layer in multicoat lacquer coatings instead of the conventional two-coat base lacquer/clear lacquer structure.

Various embodiments of each of modules A) to E) may be prepared.

35 In addition to the stated modular system, the invention also relates to a process for the production of aqueous coating compositions by mixing at least one aqueous binder

component with further coating composition components, which process is characterised in that a supply of at least one storage-stable binder module A), together with at least one storage-stable colour module B), effect module C), 5 crosslinking module D) and/or rheological module E), is prepared and optionally stored, the modules being separately prepared, wherein the individual modules are mixed together as required in a quantities such that the 10 solids content arising therefrom, relative to the total solids content of the coating compositions, assumes the following percentages:

binder modules A): 5 - 99 wt.%
colour modules B): 0 - 60 wt.%
15 effect modules C): 0 - 50 wt.%
crosslinking modules D): 0 - 50 wt.% and
rheological modules E): 0 - 50 wt.%

wherein the sum of the percentages should amount to 100%.
20 In particular, aqueous coating compositions with a solids content of 10 to 80 wt.% at application viscosity are produced. The invention also relates to the aqueous coating compositions produced in accordance with the process
25 according to the invention.

According to a preferred embodiment, the binder module A) used according to the invention contains 10-99 wt.% of the cationically stabilised (meth)acrylic copolymer, 2-70 wt.% 30 of the cationically stabilised polyurethane resin and 0.2-60 wt.% of the cationically stabilised (meth)acrylated polyurethane resin, wherein the stated percentages relate to the total binder solids content in the binder module and should add up to 100%.

35 Cationically stabilised water-dilutable binders, optionally combined with non-ionically stabilised water-dilutable

binders are prepared in at least a proportion of the modules prepared according to the invention. "Cationically stabilised" should here and below also be taken to mean the term "cationically and additionally optionally 5 non-ionically stabilised". The term "water-dilutable" used here should also be taken to mean "water-soluble". The binders may in general be, for example, (meth)acrylic copolymers, polyurethane resins or (meth)acrylated polyurethane resins which have basic groups which form 10 cationic groups by at least partial neutralisation. The binders may be self or extrinsically crosslinking. These binders and the specific examples of these binders stated below are, as mentioned, generally usable in the modules according to the invention; they are particularly 15 conveniently suitable for binder module A).

Cationic (meth)acrylic copolymers, polyurethane resins and/or (meth)acrylated polyurethane resins may, for example, be those with a number average molecular weight 20 (M_n) of 500 to 500000, an OH value of 0 to 450, an amine value of 20 to 200 and a glass transition temperature of -50°C to +150°C.

Examples of such cationic resins are described in 25 DE-A-41 34 301, DE-A-40 11 633, DE-A-41 34 290 and DE-A-42 03 510.

The (meth)acrylic copolymer resins containing basic groups preferably have an OH value of 30-200, a number average 30 molecular weight (M_n) of 1000 to 200000 and an amine value of 15-150, particularly preferably an amine value of 25-100. On neutralisation, they are preferably present in aqueous systems at a pH value of 5 to 7. Particularly preferred (meth)acrylic copolymer resins have a number 35 average molecular weight (M_n) of 4000 to 50000, a hydroxyl value of 60 to 175, an amine value of 20 to 100 and a glass transition temperature of -20 to +75°C. They may be

produced, for example, by solution polymerisation or emulsion polymerisation or copolymerisation using prior art methods, as for example described in DE-A-15 46 854, DE-A-23 25 177 or DE-A-23 57 152. They are produced, for 5 example, from (meth)acrylate monomers, optionally together with further free-radically polymerisable monomers. The free-radically polymerisable monomers, i.e. the (meth)acrylate monomers and/or further free-radically polymerisable monomers are at least in part monomers 10 containing amino groups or free-radically polymerisable monomers which may contain both amino groups and hydroxyl groups. They may be used mixed with other free-radically polymerisable monomers.

15 The method here is preferably to use 6 to 40 parts by weight of free-radically polymerisable monomers containing amino groups and 4 to 50 parts by weight of free-radically polymerisable monomers containing hydroxyl groups, or 8 to 60 parts by weight of free-radically polymerisable monomers 20 containing hydroxy and amino groups per 10 to 90 parts by weight of free-radically polymerisable monomers, which contain no further reactive groups. Of the free-radically polymerisable monomers used, preferably more than 50 wt.% and particularly preferably more than 70 wt.% are 25 (meth)acrylate monomers. These (meth)acrylate monomers may, by virtue of their ester functions, contain amino groups and/or hydroxyl groups or may occur as further non-functional monomers.

30 Suitable free-radically polymerisable monomers are virtually any ethylenically unsaturated monomers, as are common for free-radical polymerisation and which comply, for example, with Alfrey & Price's Q and e schème for copolymerisation (c.f. Brandrup & Immergut, *Polymer* 35 *Handbuch*, 2nd edition, John Wiley & Sons, New York 1975). The basic poly(meth)acrylate resins may also contain onium groups, such as quaternary ammonium groups, sulphonium or

phosphonium groups, apart from or in addition to the amino groups.

Examples of free-radically polymerisable monomers containing hydroxyl groups are (meth)acrylic acid

5 hydroxyalkyl esters, such as for example 2-hydroxyethyl acrylate, 2-hydroxypropyl methacrylate, 1,4-butanediol monoacrylate, 2,3-dihydroxypropyl methacrylate, pentaerythritol monomethacrylate, polypropylene glycol monoacrylate, adducts of (meth)acrylic acid and glycidyl 10 esters, for example of versatic acid or also fumaric acid dihydroxyalkyl esters.

N-hydroxyalkyl (meth)acrylamide or N-hydroxyalkylfumaric acid mono- or diamides such as, for example, N-hydroxymethyl-acrylamide or

15 N-(2-hydroxypropyl)methacrylamide may, however, also be used. Particularly elastic properties may be achieved by using a reaction product of hydroxyalkyl (meth)acrylates with ϵ -caprolactone. Other compounds containing hydroxyl groups are allyl alcohol, monovinyl ethers of polyalcohols, 20 in particular of diols, such as for example the monovinyl ethers of ethylene glycol or butanediol, together with allyl ethers or esters containing hydroxyl groups, such as 2,3-dihydroxypropyl monoallyl ether, trimethylolpropane monoallyl ether or 2,3-dihydroxypropanoic acid allyl ether. 25 Hydroxyethyl, hydroxypropyl and/or 1,4-butanediol mono(meth)acrylate are particularly suitable.

Monomers containing amino groups which may be used are, for example, monomers of the general formula

30 $R - CH = CH' - X - A - N(R'')_2$

wherein

R means $-R'$ or $-X-C_nH_{2n+1}$,

R' means $-H$ or $-C_nH_{2n+1}$ and

35 R'' means $-R'$, $-C_nH_{2n}OH$ and/or $-C_nH_{2n}NR_2$, wherein R is defined as above, and

X means $-COO-$, $-CONH-$, $-CH_2O-$ or $-O-$,

A means $-C_nH_{2n}-$ or $-C_nH_{2n}-CHOH-CH_2$ and
n means 1 to 8, preferably 1 to 3.

Examples of unsaturated monomers containing N groups are

5 N-dialkyl- or N-monoalkylaminoalkyl (meth)acrylate or the corresponding N-alkanol compounds, such as for example N-diethylaminoethyl acrylate or N-tert.-butylaminoethyl acrylate, N-dialkyl- or N-monoalkylaminoalkyl (meth) - acrylamide or the corresponding N-alkanol compounds, such as for example N-dimethylaminoethanolacrylamide and/or heterocyclic compounds containing vinyl groups with one or more basic nitrogen atoms, such as for example N-vinylimidazole.

15 Component A) aminopoly(meth)acrylate resins may also, as described in DE 40 11 633, be produced by a polymer-analogous reaction. A copolymer containing acrylamide groups may thus, for example, be reacted with formaldehyde and a secondary amine and/or aminoalcohol. A particularly preferred process is described in DE-A-34 36 346. In this process, monoethylenically unsaturated monomers containing epoxide groups are initially copolymerised to yield the copolymer. The product is then reacted with excess ammonia, primary and/or secondary monoamines and/or

20 monoaminoalcohols and the amine excess then removed by distillation.

25

A further suitable group of binders comprises, for example, cationically or cationically/non-ionically stabilised polyurethanes. These may be synthesised from any conventional structural units known to the person skilled in the art. For example, during production of polyurethane resins, the equivalent ratio of the diisocyanate used is adjusted relative to the polyols and diols used in such a manner that the complete polyurethane resin preferably has a number average molecular weight (M_n) of 3000 to 200000, particularly preferably of 10000 to 40000 and an amine

value of 15 to 120, particularly preferably of 20 to 100. The pH value is preferably adjusted to 5 to 7 on neutralisation.

- 5 Urethanised polyesters, which may also be hydroxy-functional, constitute a preferred group of basic polyurethane resins, wherein, for example, basic groups in the form of amino groups are either directly condensed into the polyesters as aminoalcohols or, under milder
- 10 conditions, are incorporated into the polymer chain by polyaddition or attached to the polymer chain. Thus, for example, a preferably linear polyester containing OH groups is synthesised by reacting the polyester with dialkyl-aminodialcohols and diisocyanates. If the reaction is
- 15 performed with a substoichiometric quantity of isocyanate, the resin, once neutralised with acids, must be directly dispersible in water. If, on the other hand, an isocyanate excess is used, the resultant NCO prepolymer may be dispersed in water and converted into a polyurethane(urea)
- 20 dispersion by chain extension with a polyamine. Such polyurethane(urea) dispersions may also be used according to the invention as polyurethane resins.

- 25 Polyurethane(urea) dispersions containing basic groups are produced in a known manner, for example by chain extension of a cationic prepolymer having a terminal isocyanate group with polyols, polyamines and/or hydrazine compounds, wherein chain extension is performed before or after neutralisation of the tert.-amino groups with these in
- 30 water. The amine value is controlled by the quantity of compounds containing cationic groups in the prepolymer containing isocyanate groups used during production. Particle size is dependent upon the molecular weight of the polyol used, for example OH polyester (polyester polyol),
- 35 the amine value and the sequence of synthesis. Number average molecular weight is preferably between 3000 and 500000, particularly preferably above 5000 and below 50000.

Polyurethane dispersions containing urea groups are preferably produced which contain at least 2, preferably 4 urethane groups and at least one tert.-amino group, especially a dialkylamine group in the NCO prepolymer.

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A detailed description of the production of the polyurethane and polyurethane(urea) dispersions discussed above is given, for example, in DE-A-41 34 301 and DE-A-40 11 633.

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Further binders which may readily be used in the binder module are those in which a cationic polyurethane resin and a (meth)acrylic copolymer are combined together in the form of interpenetrating resin molecules.

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(Meth)acrylated polyurethane dispersions constitute a further group for the binder module A) which are also suitable for formulating effect modules. These are, for example, so-called polymer dispersions which are obtained 20 by emulsion polymerisation of (meth)acrylic monomers in polyurethane dispersions, which are cationically and/or non-ionically stabilised. The (meth)acrylic monomers used may also contain cationic groups, groups convertible into cationic groups (such as amino groups) and/or non-ionic 25 hydrophilic groups; such monomers may be used not only to stabilise already stabilised polyurethane dispersions, but also to stabilise polyurethanes which themselves do not yet contain any stabilising groups. Particularly preferred polyurethane dispersions are those which are copolymerised 30 by emulsion polymerisation of so-called polyurethane macromers, i.e. polyurethanes with covalently attached terminal and/or lateral vinyl groups, with unsaturated monomers, preferably (meth)acrylic acid derivatives. The amine value of such dispersions is from 5-150, preferably 35 from 10-100; the hydroxyl value from 0-150, preferably from 15-120.

According to a preferred embodiment, mixtures are used as the binder for the binder module A) which contain (meth)acrylic copolymers, as described above, and polyurethane resin. Suitable (meth)acrylate copolymers are 5 in particular those described above with an OH value of 30 to 200, a number average molecular weight (M_n) of 100 to 200000 and an amine value of 15 to 150. Suitable polyurethane resins are in particular those described above with a number average molecular weight (M_n) of 3000 to 10 200000 and an amine value of 15 to 120. These mixtures are also preferably present in the binder module at a pH value of 5 to 7.

In the cationically stabilised binders used according to 15 the invention, solubility may be influenced by the number of amino groups. The amine value should preferably be 20 to 200 mg KOH/g of solid resin, preferably between 30 and 150. Primary, secondary and/or tertiary amino groups may be present. Tertiary amino groups are preferred.

20 The hydroxyl value influences crosslinking density. It should preferably be between 20 and 400. Each binder molecule should here preferably contain an average of at least two reactive groups, for example OH or NH groups. 25 Reactivity is influenced by the nature of the groups, thus primary amino or hydroxyl groups are more reactive than secondary groups, wherein NH groups are more reactive than OH groups. It is preferred for the binder to contain reactive amino groups. The binders according to the 30 invention may bear further attached crosslinkable groups, for example blocked isocyanate groups, alkoxy silane groups or transesterifiable groups. In this case, these are self crosslinking binders. It is, however, possible additionally to mix crosslinking agents into the binders. The molecular 35 weight (M_n) of the crosslinking agents is, for example, 500 to 20000, in particular 1000 to 10000. The crosslinking

agents may be present either directly in the binder module A) or in a separate crosslinking module (D).

The cationic binders may be physically drying, self or extrinsically crosslinking; this applies in particular to the cationic binders contained in binder module A). The cationic binders may contain attached crosslinkable groups, for example blocked isocyanate groups or transesterifiable groups. In this case, these are self crosslinking binders.

10 It is, however, possible to add additional crosslinking agents in a separate crosslinking module.

The modules, in particular binder module A) may optionally also contain non-ionically stabilised binders.

15 Examples of suitable non-ionically stabilised binders are those binders in which water-dilutability is achieved by incorporating polyether segments into the resin molecule. Examples of such stabilised resins are polyurethane or

20 polyurethane acrylate resins, as are described in EP-A-0 354 261, EP-A-0 422 357 and EP-A-0 424 705.

The binder module A) necessarily contained in the modular system according to the invention may contain an aqueous

25 binder, but a combination of aqueous binders may also be present. The binders may here each be separately produced and then stored as individual modules or a mixture of the binders is produced and then stored as one or more multicomponent binder modules.

30 Binder module A) may contain rheological control agents and small proportions of conventional solvents, preferably less than 5 wt.%. The solids content of the binder module is preferably 10-50 wt.%, particularly preferably 15-40 wt.%.

35 Binder module A) contains neutralising agents for the basic resins. These are acids, preferably organic monocarboxylic

acids, such as for example formic acid, acetic acid, propionic acid. Hydroxycarboxylic acids are in particular well suited, such as for example lactic acid, glycolic acid, diglycolic acid, malic acid, citric acid, mandelic acid, tartaric acid, hydroxypropionic acid, dimethylol-propionic acid. The neutralising agents are added in the desired quantity to achieve water-compatibility or water-solubility. Neutralisation may be complete or partial. The pH value in binder module A) is preferably 5 to 7.

Colour module B) is an aqueous preparation which contains one or more coloured pigments and/or extenders, one or more cationically stabilised polyurethane paste resins, water 15 optionally together with water-dilutable cationic binders optionally combined with non-ionically stabilised binders, one or more organic solvents and/or conventional lacquer additives. Water is present in a quantity of at least 6 wt.%, preferably of at least 10 wt.%.

20 Each colour module B) preferably contains no more than four different coloured pigments and/or extenders, the aqueous colour modules particularly preferably contain only one coloured pigment or only one extender. The colour modules 25 of the systems according to the invention may contain conventional inorganic and/or organic coloured pigments and/or extenders as well as transparent pigments. Examples of inorganic or organic coloured pigments or extenders are titanium dioxide, micronised titanium dioxide, iron oxide 30 pigments, carbon black, silicon dioxide, barium sulphate, micronised mica, talcum, azo pigments, phthalocyanine pigments, quinacridone or pyrrolopyrrole pigments.

Cationically stabilised polyurethane paste resins which may 35 be used in the colour module preferably have a solids content (relative to the total weight of the colour module) of 20-50 wt.%, a viscosity of 0.5-50 mPa·s at 25°C and are

preferably 70 to 100% neutralised with monocarboxylic acids. Examples of suitable monocarboxylic acids are those already stated above in the description of the binder module.

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Polyurethane paste resins preferably used in the colour module B) are, for example, basic polyesterurethane resins during the production of which the equivalent ratio of the diisocyanate used is adjusted relative to the polyols and 10 diols used in such a manner that the complete polyurethane resin, for example polyesterurethane resin, has a number average molecular weight (M_n) of 3000 to 200000, preferably of below 50000. The OH value is preferably 0 to 80, particularly preferably 10 to 65; the amine value is 15 preferably 15 to 150, particularly preferably 10 to 100. The ratio of the OH groups of the polyol, for example polyester polyol and diol, to the NCO groups of the 20 isocyanates is preferably maintained above 1.0 to 1.2:1; the viscosity of the polyurethane resin, for example polyesterurethane resin, is preferably 1 to 30 Pa·s, particularly preferably above 2 and below 15 Pa·s, measured as a 60% solution in butoxyethanol at 25°C.

The colour module B) which may be used according to the 25 invention may, in addition to the basic polyurethane paste resin, contain cationically stabilised water-dilutable binders, optionally combined with non-ionically stabilised binders. These may, for example, be the same resins as have already been described in binder module A). Other 30 cationically stabilised binders may, however, also be included, for example polyester resins.

The colour module B) may furthermore contain small proportions of at least one water-miscible solvent, such as 35 alcohols, for example monoalcohols, such as butanol, n-propanol, isopropanol; ether alcohols, for example butoxyethanol, butoxypropanol, methoxypropanol, dialcohols,

such as glycols, for example ethylene glycol, polyethylene glycol; trialcohols such as glycerol; ketones, for example acetone, methyl ethyl ketone; N-methylpyrrolidone; ethers, for example dipropylene glycol dimethyl ether.

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The module may, as already described in A), also contain acids as neutralising agents. Examples are organic monocarboxylic acids, such as for example formic acid, acetic acid, dimethylolpropionic acid.

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It may be favourable for the colour module B) to contain one or more rheological control agents. These may, for example, be substances or mixtures as are described in the production of the rheological module E). These may be added 15 directly during production of the colour module or subsequently mixed in as a complete rheological module.

The colour module B) containing water may furthermore contain conventional lacquer additives, such as for example 20 wetting agents, defoaming agents, levelling agents, dispersion auxiliaries.

The colour module B) containing water is generally produced in such a manner that the coloured pigment and/or extender 25 is ground in the paste resin. The paste resin may be present in un-neutralised, partially neutralised or completely neutralised form in an organic, at least partially water-miscible solvent or in an aqueous solution or dispersion. Solutions or dispersions containing water 30 are preferred. This may proceed in conventional apparatus familiar to the person skilled in the art. The module is then optionally formulated with a further proportion of paste resin and/or the cationically and optionally non-ionically stabilised water-dilutable binders optionally 35 contained in the colour module (B) and/or further additives.

Storage-stable, aqueous colour modules (B) are obtained with a pigment or extender:binder ratio of, for example, 0.01:1 to 10:1, relative to solids weight. Solids content is preferably 20-80 wt.%.

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The water content in the colour module is preferably at least 6 wt.%, particularly preferably at least 10 wt.%.

10 The effect module C) is an aqueous preparation which contains at least one or more effect pigments and water, optionally together with one or more organic solvents, one or more cationically stabilised water-dilutable (meth)acrylated polyurethane resins, which may be present combined with non-ionically stabilised water-dilutable 15 binders, optionally together with one or more organic solvents and conventional lacquer additives.

20 Effect pigments are those pigments which bring about a decorative effect in lacquer coatings and additionally, but not exclusively, may bring about a coloured effect. Effect pigments are in particular distinguished by a lamellar structure. Examples of effect pigments are: metal pigments, for example made of aluminium, copper or other metals; interference pigments, such as for example metal pigments 25 coated with metal oxides, for example aluminium coated with titanium dioxide or mixed oxide, coated micas, such as for example mica coated with titanium dioxide and graphite effect pigments.

30 Many such effect pigments varying in particle size and shape are commercially available. The pigments are selected on the basis of the desired effect in the lacquer film. Preferably, effect modules are produced with only one pigment. It is, however, possible for effect modules to 35 contain two or more different effect pigments.

The effect module may moreover contain small proportions of at least one water-miscible solvent, as for example described in A), such as alcohols, for example monoalcohols, such as butanol, n-propanol; ether alcohols, 5 for example butoxyethanol, butoxypropanol, methoxypropanol; dialcohols, such as glycols, for example ethylene glycol, polyethylene glycol; trialcohols such as glycerol; ketones, for example acetone, methyl ethyl ketone, N-methyl-pyrrolidone; ethers, for example dipropylene glycol 10 dimethyl ether.

Examples of water-dilutable cationically stabilised (meth)acrylated polyurethanes usable in the effect module C) are those as were in particular described above for the 15 binder module A) as (meth)acrylated polyurethane dispersions, in particular with an amine value of 5 to 150, preferably of 10 to 100 and a hydroxyl value of 0 to 150, preferably of 15 to 120.

20 The effect module may contain rheological control agents. These may, for example, be substances or mixtures as are described below in the description of the rheological module E).

25 These may be added directly during production of the colour module or subsequently mixed in as a complete rheological module.

30 The aqueous effect module may furthermore contain conventional lacquer additives, such as for example wetting agents, defoaming agents, neutralising agents, catalysts.

35 The effect module containing water is generally produced in such a manner that the effect pigment, for example in the form of a conventional commercial paste, is initially introduced into a vessel, combined with water-dilutable

organic solvents and additives and optionally subsequently mixed with the aqueous resin solution with shearing.

Storage-stable, aqueous effect modules are obtained with a 5 preferred pigment:binder weight ratio of 0.02:1 to 10:1. The solids content of the entire effect module is preferably 10-40 wt.%. The water content in the effect module is at least 6 wt.%, particularly preferably at least 10 wt.%.

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The modular system according to the invention may also contain a crosslinking module D). The crosslinking module D) is in particular used in the event that the coating composition to be prepared is produced using those resins 15 which contain crosslinkable groups in their molecule. Examples of crosslinking resins contained in the crosslinking module are conventional crosslinking agents, such as polyisocyanates, polyamines, blocked polyisocyanates, amino resins, phenolic resins, 20 crosslinking agents containing siloxane groups and/or transesterification crosslinking agents.

The polyisocyanates may be any desired organic polyisocyanates with aliphatically, cycloaliphatically 25 and/or aromatically attached free isocyanate groups. They are liquid at room temperature or liquefied by the addition of organic solvents. At 23°C, the polyisocyanates have a viscosity of, for example, 1 to 6000 mPa·s, preferably of above 5 and below 3000 mPa·s.

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Such polyisocyanates are generally known and described, for example, in DE-A-38 29 587 or DE-A-42 26 243.

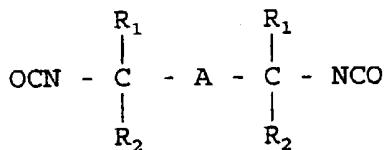
The polyisocyanates are preferably polyisocyanates or 35 polyisocyanate mixtures with exclusively aliphatically and/or cycloaliphatically attached isocyanate groups with

an average NCO functionality of 1.5 to 5, preferably of 2 to 3.

Particularly suitable compounds are, for example, "lacquer 5 polyisocyanates" based on hexamethylene diisocyanate, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI) and/or bis(isocyanatocyclohexyl)methane and the *per* se known derivatives of these diisocyanates with biuret, allophanate, urethane and/or isocyanurate groups, from 10 which the excess starting diisocyanate has been removed after production, preferably by distillation, down to a residual content of less than 0.5 wt.%.

Sterically hindered polyisocyanates of the general formula

15



20

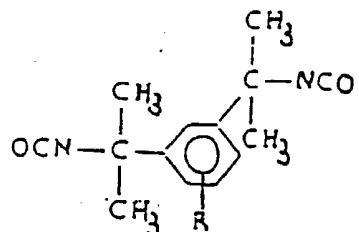
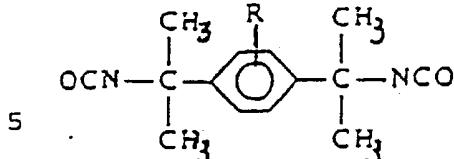
are also very suitable, wherein

R_1 is H or R_2 ,

25 R_2 is $\text{C}_n\text{H}_{2n+1}$ with
n being 1 to 6.

Substituents R_1 and R_2 are either linear or branched, 30 identical or different. The parent structure A may consist of a single bond, an aromatic or alicyclic ring or an aliphatic linear or branched C chain with 1 to 12 C atoms.

Examples of such substances are 1,1,6,6-tetramethyl-35 hexamethylene diisocyanate, 1,5-dibutylpentamethyl-diisocyanate, p- or m-tetramethylxylylene diisocyanate of the general formula



in which R means H or C₁-C₄ alkyl, and the corresponding hydrogenated homologues, together with 2,3-bis-(8-
 10 isocyanatoethyl)-4-octyl-5-hexylcyclohexane and
 3(4)-isocyanatomethyl-1-methylcyclohexyl isocyanate. These diisocyanates may also be reacted in a suitable manner to yield more highly functional compounds, for example by trimerisation or by reaction with water or trimethylol-
 15 propane.

Examples of blocked isocyanates are any desired di- and/or polyisocyanates in which the isocyanate groups are reacted with a compound containing active hydrogen. Corresponding
 20 prepolymer containing isocyanate groups may also be used as the di- and/or polyisocyanates. These are, for example, aliphatic, cycloaliphatic, aromatic, optionally also sterically hindered polyisocyanates, as have already been described above by way of example. Trifunctional, for
 25 example tri- to pentafunctional aromatic and/or aliphatic blocked isocyanates with a number average molecular weight of 500-1500 are preferred.

Conventional blocking agents may be used. Thus, for
 30 example, low molecular weight compounds containing acidic hydrogen are known for blocking NCO groups. Examples of such compounds are aliphatic or cycloaliphatic alcohols, dialkylaminoalcohols, oximes, lactams, heterocyclics containing NH groups, such as for example pyrazoles or
 35 triazoles, imides, hydroxyalkyl esters, esters of malonic acid or acetoacetic acid.

Amino resins are also suitable as crosslinking resins. Amino resins are described, for example, in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th edition, volume A2, *Amino resins* entry, pages 115-141 (1985) and

5 Houben-Weyl, *Methoden der Organischen Chemie*, volume 14/2, pages 319-399 (1962). The resins are produced in accordance with the prior art and offered for sale by many companies as commercial products.

10 Examples of such amino resins are amine/formaldehyde condensation resins, which are produced by the reaction of aldehydes with melamine, guanamine, benzoguanamine or dicyanodiamide. The alcohol groups of the aldehyde condensation products are then partially or completely

15 etherified with alcohols.

Further examples of crosslinking agents which may also be contained in the crosslinking module are conventional transesterification crosslinking agents.

20 Transesterification crosslinking agents are polyesters containing no carboxyl groups with lateral or terminal β -hydroxyalkyl ester groups. These are esters of aromatic polycarboxylic acids, such as for example isophthalic acid, terephthalic acid, trimellitic acid or mixtures thereof.

25 These are condensed, for example, with ethylene glycol, neopentyl glycol, trimethylolpropane and/or pentaerythritol. The carboxyl groups are then reacted with optionally substituted 1,2-glycols to form β -hydroxyalkyl compounds. The 1,2-glycols may be substituted with

30 saturated or unsaturated alkyl, ether, ester or amide groups. The formation of hydroxyalkyl esters is also possible in which the carboxyl groups are reacted with substituted glycidyl groups, such as for example glycidyl ethers and glycidyl esters.

35 The transesterification crosslinking agents preferably contain more than 3 β -hydroxyalkyl ester groups per

molecule and have a weight average molecular weight of 1000 to 10000, preferably of above 1500 and below 5000. The polyesters containing no carboxyl groups with lateral and terminal β -hydroxyalkyl ester groups may be produced as is 5 described, for example, in EP-A-0 012 463.

Polyamine crosslinking agents suitable as crosslinking resins are, for example, diamines and amines with more than 10 two amino groups, wherein the amino groups may be primary and/or secondary. Suitable polyamines are also adducts consisting of polyamines with at least two primary amino groups and which may be modified by further functional groups, for example with epoxy groups, with polyisocyanates or with (meth)acryloyl compounds. Polymers into which the 15 amino-functional groups are only subsequently introduced by reaction are also suitable as polyamines.

Examples of suitable polyamines are described in EP-A-0 240 083 or EP-A-0 346 982. Examples of these are 20 aliphatic and/or cycloaliphatic amines with 2-24 atoms, which contain 2-10 primary amino groups and 0-5 secondary amino groups. Examples of these are hexamethylenediamine, 1,2-diaminocyclohexane, isophoronediamine, diethylene-triamine or polyether polyamines.

25 Examples of conventional polyamines based upon modified polyfunctional amine components with di- or polyfunctional epoxy compounds are those produced using, for example, diglycidyl or polyglycidyl ethers based on bisphenol A or 30 bisphenol F, polyglycidyl ethers of phenolformaldehyde or novolaks; glycidyl ethers of fatty acids with 6-24 C atoms, epoxidised polybutadienes or resins containing glycidyl groups, such as polyesters or polyurethanes, which contain one or more glycidyl groups per molecule.

35 Polyamidoamines may also be used, as are, for example, described in EP-A-0 262 720. These are reaction products

prepared from mono- or polycarboxylic acids with polyamines which contain primary amino groups.

Polyamine/isocyanate adducts may also be used. Suitable 5 isocyanates for this purpose are the aliphatic, cycloaliphatic and/or aromatic di- or polyisocyanates conventional in the lacquer sector.

Further methods for the synthesis of amino-functionalised 10 curing agents are described in EP-A-0 002 801 and in EP-A-0 179 954. These are copolymers based on (meth)acrylic acid derivatives which are reacted and functionalised with diamines or alkyleneimines.

15 The crosslinking module D) may contain the crosslinking agent alone. It may, however, also contain one or more organic solvents, water and/or conventional lacquer additives. These are, for example, the same solvents and additives as are described for the other modules. The 20 module may in particular contain catalysts which accelerate the reaction between the binder and crosslinking component.

When amine/formaldehyde resins are used, the catalysts used are, for example, amine salts or readily hydrolysable 25 esters of organic sulphonic acids or sulphonamides, as may be obtained as conventional commercial products. In the event of a combination with polyisocyanates, organometallic compounds, such as dibutyltin dilaurate may be used, optionally combined with basic catalysts, such as 30 1,4-diazabicyclo[2.2.2]octane.

The modular system according to the invention may also contain a rheological module E). This preferably contains water and, as the rheological component, one or more 35 substances controlling the flow properties of the finished aqueous effect base lacquer.

Examples thereof are polymer microparticles, as are for example described in EP-A-0 038 127, inorganic phyllosilicates, for example aluminium-magnesium silicate, sodium-magnesium phyllosilicates and sodium-magnesium-
5 fluorolithium phyllosilicates of the montmorillonite type, associative thickeners, for example based on polyurethane or cellulose, polyvinyl alcohol, poly(meth)acrylamide, polyvinylpyrrolidone and polymeric urea compounds, synthetic polymers with ionic groups, such as for example
10 poly(meth)acrylic acid. These substances are commercially available in many forms.

Polyurethane-based cationic associative thickeners are preferred here.

15 The polyurethane-based associative thickeners are resins having the following schematic structure: hydrophilic segments such as polyether structures (wherein these preferably contain a proportion of ethylene oxide units, 20 preferably of 35% or more, in the event that only polyether structures are present) and/or cationic groups or groups convertible into cations are incorporated into the main polymer chain. In contrast, long-chain hydrophobic components are incorporated onto the chain ends. They are 25 responsible for the thickening action of such systems. They are synthesised in a similar manner to the polyurethane synthesis methods already described. Any usual starting materials for polyurethane synthesis available to the person skilled in the art are suitable for this purpose.
30 Long-chain fatty alcohols and fatty amines are preferably used as the hydrophobic modifiers. These contain, for example, a linear chain with at least 8, preferably at least 12 carbon atoms, wherein crosslinked fractions are also possible.

35 The amine value of associative thickeners is preferably 5 to 100, particularly preferably 10 to 90; the hydroxyl

value is 0 to 70, preferably 5 to 50. Naturally, in accordance with the conventional definition, the amine value and OH value in the present description each relate to mg of KOH per g of solid resin.

5

The various modules are stable in storage. Two or more identical or different modules may be mixed to yield novel storage-stable combined modules. Various effect and/or colour modules may, for example, be mixed together.

10

The invention provides an advantageous process for the production of various types of aqueous coating compositions based on a standard binder, which process is characterised in that a supply of each of the modules A) to E) according 15 to the invention is prepared and optionally stored, the modules being separately prepared, and, when required, the modules necessary for a particular application, such as for example the quantities required to achieve a desired colour tone or effect, of the prepared modules A) are mixed with 20 B) and/or C) and/or D) and/or E).

The aqueous coating compositions are produced by simply mixing the binder modules A) with the colour modules B), the effect modules C), the crosslinking modules D) and/or 25 the rheological modules E). Depending upon the selection of the second necessary modular component or the further possible modular components, various coating compositions may be produced, such as base lacquers, single-coat topcoat lacquers or clear lacquers.

30

Thus, for example, in order to produce clear lacquers, at least one binder module and at least one crosslinking module are mixed together. The binder modules used here are preferably based upon a binder combination of cationic 35 (meth)acrylic copolymer resins and cationic polyester-polyurethane resins. The preferred resins for this purpose are those described above for the binder module A).

Particularly preferred poly(meth)acrylate resins have a number average molecular weight (M_n) of 4000-50000, a hydroxyl value of 60-175 mg KOH per g of solid resin and a glass transition temperature of -20 to +75°C. The amine 5 value is preferably 20-100 mg KOH per g of solid resin. The crosslinking module preferably contains those crosslinking agents based on blocked or unblocked polyisocyanates and/or melamine resins with at least two groups per molecule which are reactive towards amino and/or OH groups.

10

In order to produce clear lacquers, the modular system according to the invention preferably contains at least one rheological module. It is possible by means of a separate rheological module subsequently to influence rheology 15 during production of the coating composition. If the rheological agents are, for example, already contained in the binder module A), then the rheology of the complete coating composition is predetermined by the binder. The rheological agents used here are preferably 20 polyurethane-based cationic associative thickeners, as have already been stated in the description of the rheological module.

The modular system may also contain transparent pigments, 25 for example transparent titanium dioxide, for the production of clear lacquers. The transparent pigments may be contained in a separate colorant module or in one of the other modules present.

30 A modular system according to the invention for the production of, in particular, effect base lacquers, preferably consists of a binder module A) based on a binder combination prepared from a cationic poly(meth)acrylate resin and a cationic polyurethane resin and an effect 35 module C) with a (meth)acrylated polyurethane dispersion as the binder and optionally a colour module B) with preferably one or more cationically stabilised polyester-

urethane resins as the binder together with a rheological module E) with preferably polyurethane-based cationic associative thickeners. The resins preferably used here are described in the binder module.

5

In order to produce, in particular, single-tone base lacquers and single-tone, single-coat topcoat lacquers, the modular system according to the invention may preferably contain at least one binder module A) based on a binder 10 combination prepared from a cationic poly(meth)acrylate resin and a cationic polyesterurethane resin, at least one colour module, wherein the colour module preferably contains the cationic polyurethane paste resins described above, and a rheological module based on polyurethane-based 15 cationic associative thickeners. A crosslinking module may be present in both the single-tone base lacquers and the single-tone, single-coat topcoat lacquers, which module contains, for example, melamine resin crosslinking agents and/or blocked polyisocyanates. Preferred resins are 20 described above in the binder and rheological modules.

The modules may be added in any desired sequence during production of the coating compositions. Preferably, however, the modules with the highest viscosities and the 25 highest proportions by volume are introduced initially. After mixing, application viscosity may be established by adding deionised water.

The coating compositions produced from the modular system 30 according to the invention preferably have a solvent content of below 20 wt.%, particularly preferably of below 10 wt.%.

The complete coating compositions may be applied directly 35 after mixing. They may, however, also be stored for longer than 12 months. In the case of room temperature

crosslinkable two-component coating compositions, the crosslinking module must, however, be separately stored.

A particular advantage of the modular system according to 5 the invention is that the most varied coating compositions may be prepared in a simple manner from standard components. The present invention also provides these coating compositions.

10 The quantities listed below may, for example, here be used in the production of the coating compositions according to the invention. The quantities relate to the solids contents from the individual modules, which make up the total solids content of the coating composition (100 wt.%).

15 When producing aqueous effect base lacquers, the solids content from the binder module is preferably 10 to 99, particularly preferably 40 to 95 wt.%; the solids content from the colour module 0 to 40, preferably 0 to 30 wt.%; 20 the solids content from the effect module preferably 0.01 to 50, particularly preferably 1 to 30 wt.%; the solids content from the crosslinking module 0 to 40, preferably 0 to 25 wt.% and the solids content from the rheological module preferably 0.01 to 50, particularly preferably 1 to 25 40 wt.%. In order to achieve application viscosity, the aqueous effect base lacquer is preferably adjusted to a total lacquer solids content of 10 to 55 wt.%, particularly preferably of 12 to 40 wt.%.

30 When producing single-tone aqueous base lacquers, the solids content from the binder module is preferably 5 to 60 wt.%, particularly preferably 8 to 50 wt.%; from the colour module preferably 1 to 60, particularly preferably 3 to 50 wt.%; from the crosslinking module 0 to 40, 35 preferably 0 to 25 wt.% and from the rheological module 0 to 40, preferably 1 to 30 wt.%. The solids content of the single-tone aqueous base lacquer is adjusted to application

viscosity with a solids content of preferably 10 to 60 wt.%, particularly preferably of 12 to 45 wt.%.

In order to produce single-coat topcoat lacquers, the
5 solids content from the binder module is preferably 5 to 60 wt.%, particularly preferably 8 to 50 wt.%; the solids content from the colour module preferably 0.5 to 60 wt.%, particularly preferably 1 to 45 wt.%; from the effect module 0 to 50 wt.%, preferably 0 to 30 wt.%; from the
10 crosslinking module preferably 0.5 to 40 wt.%, particularly preferably 1 to 35 wt.% and from the rheological module 0 to 40 wt.%, preferably 1 to 30 wt.%. At application viscosity, the total solids content of the single-coat topcoat lacquer is preferably 10 to 70 wt.%, particularly
15 preferably 12 to 50 wt.%.

When producing clear lacquers, the solids content from binder module is preferably 15 to 90 wt.%, particularly preferably 35 to 85 wt.%; from the colour module 0 to 20, 20 preferably 0 to 10 wt.%; from the effect module 0 to 10, preferably 0 to 5 wt.%; from the crosslinking module preferably 0.01 to 50 wt.%, particularly preferably 2 to 40 wt.%; from the rheological module 0 to 40 wt.%, particularly preferably 1 to 30 wt.%. At application
25 viscosity, the total lacquer solids content of the clear lacquer is preferably 10 to 80 wt.%, particularly preferably 12 to 65 wt.%.

The aqueous coating compositions produced from the modular system according to the invention may be applied using conventional methods, for example by spraying. Curing may proceed at, for example, between 20°C and 140°C.

A preferred option for application is to apply a base
35 lacquer produced with the modular system according to the invention and, after a flashing-off stage at 20°C-80°C, to apply a conventional clear lacquer or a clear lacquer

produced with the modular system according to the invention using the wet-on-wet method and curing both layers together.

5 The multicoat lacquer coatings obtained in this manner satisfy today's conventional requirements for automotive lacquer coating. They are suitable for automotive original and repair lacquer coating, but they may also be used in other sectors, for example for lacquer coating plastics,
10 wood or ceramics.

The modular system according to the invention consists of individual storage-stable modules which may simply and readily be mixed together. Low-solvent, aqueous coating
15 compositions with good long term storage stability may be produced. Storage and production of the various coating compositions, such as base lacquers, topcoat lacquers and clear lacquers, are rationalised by means of a single modular system. A particular advantage of the system
20 according to the invention and of the process according to the invention is that the most varied coating compositions may be prepared on the basis of standard modules.

The following examples are intended to illustrate the
25 invention in greater detail.

Production examples for binder

Production example 1:

966 g of ethoxypropanol are heated under inert gas to 100°C
30 with a reflux condenser being used. Within a period of 4 hours, a mixture of 195.5 g of hydroxyethyl methacrylate, 599 g of butanediol monoacrylate, 592 g of n-butyl methacrylate, 483 g of 2-ethylhexyl methacrylate, 439 g of butyl methacrylate, 439 g of methyl methacrylate, 893 g of
35 styrene, 358 g of 3'-dimethylaminopropylmethacrylamide and 46 g of t.-butyl peroctoate is added. The temperature is then maintained at 110°C for 1 hour, 8.4 g of t.butyl

perooctoate dissolved in 12.2 g of ethoxypropanol are added and this operation is repeated one hour later. After 3 hours at 110°C, the following intermediate values are determined:

5

Solids content: 79.6 (30 minutes 150°C)
Viscosity: 12.5 Pa·s (50% in ethoxypropanol at 25°C)

10 Production of the aqueous dispersion:

4 g of formic acid solution (50% in water) and 32.6 g of ethylene glycol monobutyl ether are thoroughly incorporated into 250 g of the aminoacrylate described above and 713.4 g 15 of completely deionised water are then added to produce the dispersion. After 2 hours' stirring, a finely divided aqueous aminoacrylate dispersion is obtained.

Characteristics:

20 Solids content: 20.4 wt.% (60 minutes 150°C)
Acid mEq: 21 mEq/100 g of solid resin
pH value: 6.5

Production example 2:

25 (Production example 1 in DE-A-4 011 633)

725 g of butoxyethanol are heated under inert gas to 110°C with a reflux condenser being used. Within a period of 3 hours, a mixture of 192 g of hydroxyethyl methacrylate, 30 137 g of butanediol monoacrylate, 288 g of glycidyl methacrylate, 364 g of 2-ethylhexyl acrylate, 439 g of butyl methacrylate, 439 g of methyl methacrylate, 90 g of styrene and 44 g of azobisisobutyronitrile are added. Then, after 1 hour at 110°C, a solids content of 72.2 wt.% is 35 measured and, after dilution to 60 wt.% with butoxyethanol, a viscosity of 2.14 Pa·s at 25°C is measured. After cooling to 50°C, a mixture of 120 g of diethylamine and 201 g of

isopropanol is added rapidly (1.10 mol of amine for 1.00 mol of epoxide). After 30 minutes, the temperature is raised to 65°C, maintained for 2 hours, then raised to 105 to 110°C and maintained for 3 hours. After cooling to 80°C,
5 isopropanol and excess amine are carefully removed by vacuum distillation. Solids content is adjusted to approximately 80 wt.% with butoxypropanol.

Intermediate value:

10

Solids content: 79.7% (30 minutes 150°C)
Amine value: 45 mg KOH per g of solid resin
Viscosity: 3.44 Pa·s (60% in butoxyethanol at 25°C)

15

Production example 3:

855 g of a polyester polyol (produced from neopentyl glycol, hexanediol and isophthalic acid with an OH value of 20 102 and an acid value 1) are mixed at approximately 45°C under inert gas with 138 g of methyldiethanolamine and 300 g of acetone in a reaction vessel with a stirrer, internal thermometer, heater and reflux condenser. 410.5 g of isophorone diisocyanate are then added and the 25 exothermic reaction is maintained at 80°C by cooling and heating until virtually no free isocyanate may any longer be detected (NCO value less than 0.2). At 40°C, 88.6 g of lactic acid in 200 g of water are added and thoroughly incorporated. 2902 g of completely deionised water are then 30 added to produce the dispersion. After 2 hours' stirring at room temperature, a finely divided polyurethane dispersion is obtained.

Final values:

Solids content: 34.2 wt.% (60 minutes 150°C)
Acid mEq: 66 mEq/100 of solid resin
5 pH value: 5.6

Production example 4:

912 g of a polyester (produced from adipic acid,
10 isophthalic acid, 1,6-hexanediol and neopentyl glycol with
an OH value of 113 and an acid value 1) are mixed at
approximately 45°C under inert gas with 191 g of
methyldiethanolamine and 185 g of N-methylpyrrolidone in a
reaction vessel with a stirrer, internal thermometer,
15 heater and reflux condenser. 697 g of isophorone
diisocyanate are then added and the exothermic reaction is
maintained at 80°C by cooling and heating until the NCO
value is approximately 3.3. After the addition of 185 g of
N-methylpyrrolidone, 184 g of hydroxyethyl methacrylate are
20 added and the temperature maintained at 60°C until no free
isocyanate may any longer be detected.

At 40°C, 74.1 g of formic acid in 152 g of water are added
and thoroughly incorporated. 2026 g of completely deionised
25 water are then added to produce the dispersion. After 2
hours' stirring at room temperature, a finely divided
polyurethane dispersion is obtained.

Final values:

30 Solids content: 44.0 wt.% (60 minutes 150°C)
Amine value: 45 mg KOH

Production example 5:

35 30 g of the polyurethane dispersion from production example
4 are diluted with 25 g of completely deionised water and

heated to 80°C. An emulsion prepared from 0.23 g of hexanediol diacrylate, 0.45 g of lauryl acrylate, 2.0 g of styrene, 1.2 g of ethylhexyl acrylate, 1.6 g of hydroxyethyl acrylate, 3.1 g of n-butyl methacrylate and 5 0.4 g of azoisobutyronitrile in 14 g of the polyurethane dispersion from production example 4 and 10 g of completely deionised water is added over a period of 3.5 hours at 80°C. This temperature is then maintained for one hour, then an emulsion of 0.1 g of azoisobutyronitrile in 2.3 g 10 of polyurethane dispersion from production example 4 is added and the temperature maintained at 80°C for one more hour. A finely divided dispersion with the following characteristics is obtained:

15 Solids content: 31.8 wt.% (1 hour 150°C)
Amine value: 32 mg KOH/g
pH value: 5.1

Production example 6:

20 909 g of a polycaprolactone diol with an OH value of 112 and an acid value of 1 is mixed under inert gas at approximately 45°C with 141.5 g of methyldiethanolamine in a reaction vessel with a stirrer, internal thermometer, 25 heater and reflux condenser. 442.5 g of isophorone diisocyanate are then added and the exothermic reaction is maintained at 80°C by cooling and heating until virtually no free isocyanate may any longer be detected (NCO value of less than 0.2).

30 96.5 g of lactic acid in 152 g of water are added at 60°C and thoroughly incorporated. 2759 g of completely deionised water are then added to produce the dispersion. After 2 35 hours' stirring at room temperature, a finely divided polyurethane dispersion is obtained.

Final values:

Solids content: 33.5 wt.% (60 minutes 150°C)
Amine value: 45 mg KOH
5 Acid mEq: 75 mEq/100 solid resin

Production example 7:

682.5 g of a polyester diol (produced from neopentyl
10 glycol, cyclohexanedicarboxylic acid and isophthalic acid
with an OH value of 49 and an acid value of 1.3), 27 g of
pentaerythritol, 148.3 g of dodecanol and 508 g of
N-methylpyrrolidone are mixed under inert gas at
approximately 45°C with 153 g of methyldiethanolamine in a
15 reaction vessel with a stirrer, internal thermometer,
heater and reflux condenser. 529 g of isophorone
diisocyanate are then added and the exothermic reaction is
maintained at 80°C by cooling and heating until virtually
no free isocyanate may any longer be detected (NCO value of
20 less than 0.2).

118 g of formic acid (50% in water) are added at 50°C and
thoroughly incorporated. 2828 g of completely deionised
water are then added to produce the dispersion. After 2
25 hours' stirring at room temperature, a finely divided
polyurethane dispersion is obtained.

Final values:

30 Solids content: 32.3 wt.% (60 minutes 150°C)
Acid mEq: 84 mEq/100 g solid resin
pH value: 5.2

Production examples for the individual modules:**Binder modules:**

5 The binder modules are produced by thoroughly stirring together their constituents:

Binder module I:**10 Constituents:**

172.0 g binder (according to production example 5)
28.5 g binder according to production example 3
234.5 g binder according to production example 1
15 30.0 g completely deionised water

Binder module II:**Constituents:**

20 70.4 g binder according to example 1
5.3 g binder according to example 3
4.3 g completely deionised water

25 Binder module III:**Constituents:**

30 47.3 g binder according to example 2
5.2 g binder according to example 3
3.2 g completely deionised water

Binder module IV:

Constituents:

5 31.3 g binder according to example 5
24.5 g binder according to example 2
2.5 g binder according to example 3
1.2 g ethylene glycol monobutyl ether
13.0 g completely deionised water

10

Rheological module I:

100 g of the binder according to example 7 are mixed with
2 g of ethylene glycol monobutyl ether and 10 g of
15 completely deionised water.

Effect modules:

For production of the effect modules, the particular effect
20 pigment is initially introduced into a vessel and solvents,
wetting additives and binders are then thoroughly stirred
in.

Effect module I:

25

Constituents:

8.4 g of a conventional commercial aluminium paste
 suitable for aqueous base lacquers with 65%
30 aluminium
0.8 g of an aluminium wetting additive based on organic
 phosphoric acid derivatives
4.9 g ethylene glycol monobutyl ether
2.0 g N-methylpyrrolidone
35 4.5 g n-butanol
 8.0 g binder according to production example 5

The module has a water content of 8.9 wt.%.

Effect module II:

Constituents:

5 12.8 g of a conventional commercial iodine pigment
 2.7 g of a conventional commercial wetting additive
 2.7 g n-butanol
 1.1 g N-methylpyrrolidone
 8.0 g binder according to production example 5

10

The effect module has a water content of 9.3 wt.%.

Colour modules:

15 Blue colour module:

41.1 g binder according to example 6
 1.1 g of a conventional commercial dispersion auxiliary
 0.6 g ethylene glycol monobutyl ether
20 33.9 g of a conventional commercial blue copper
 phthalocyanine pigment
 10.5 g completely deionised water

Red colour module:

25

Constituents:

44.0 g binder according to example 6
 1.6 g of a conventional commercial dispersion auxiliary
30 2.9 g ethylene glycol monobutyl ether
 34.5 g of a conventional commercial red pigment
 17.1 g completely deionised water

Black colour module:

Constituents:

5 48.9 g binder according to example 6
 1.2 g of a conventional commercial dispersion auxiliary
 5.0 g ethylene glycol monobutyl ether
 13.5 g of a conventional commercial carbon black pigment
 15.6 g completely deionised water

10 The pigment is ground in the stated mixture with an appropriate apparatus.

Crosslinking module:

15 Crosslinking module I (melamine resin mixture):

6.5 g Cymel 373
3.5 g completely deionised water

20 Crosslinking module II:

25 9.7 g Luwipal 012
 2.0 g of a conventional commercial isocyanate blocked with butanone oxime and based on isophorone diisocyanate
 1.3 g ethylene glycol monobutyl ether

Crosslinking module III:

30 3.0 g Cymel 327
 7.0 g completely deionised water

Crosslinking module IV:

35 8.1 g Setamin US 138
 6.9 g ethylene glycol monobutyl ether

Production of aqueous base lacquers

Storage-stable, aqueous effect lacquers are produced by uniformly mixing together the modules stated in the table.

5 They are adjusted to the desired application viscosity with water. The stated values are parts by weight.

Effect base lacquers:

		A Silver metallic	B Silver metallic	C Silver	D Blue metallic
10	Binder module I	68.9	71.2		
	Binder module IV			72.6	72.6
	Effect module I	15.0		15.0	15.0
	Effect module II		20.1		
15	Rheological module I	8.5	9.0	10.5	10.5
	Crosslinking module I			10	10
	Blue colour module				4

20 Single-tone base lacquers & single-tone, single-coat topcoat lacquers:

		A Blue	B Black	C Red	D Red	E Topcoat lacquer
	Binder module II	80.6	76.5	76.2		75.5
25	Binder module III				55.7	
	Rheological module I	10.4	9.6	7.8	10.4	10.5
	Crosslinking module III				10	11
	Blue colour module	10.5				13.4
	Red colour module			12.45	15.9	
30	Black colour module		14.23			

Aqueous single-tone lacquers are obtained by mixing the above-stated components. They are adjusted to the particular desired application viscosity with water.

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They may be used as aqueous base lacquers and single-tone, single-coat topcoat lacquers.

Aqueous clear lacquer

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	A	B	C	D	E
Binder module II	76.2	76.5	76.2	76.5	76.5
Thickening module I	9.0	9.6	9.0	10.2	9.6
Crosslinking module I	10				6.5
10 Crosslinking module II		13.2			
Crosslinking module III			10.0		
Crosslinking module IV				15.0	10.5

Patent Claims:

5 1. Modular system for the production of aqueous coating compositions, containing

10 A) at least one aqueous binder module containing one or more cationically stabilised water-dilutable (meth)acrylic copolymers and one or more cationically stabilised water-dilutable polyurethane resins and/or one or more cationically stabilised water-dilutable (meth)acrylated polyurethane resins, optionally combined with non-ionically stabilised water-dilutable binders, water, optionally together with one or more organic solvents and/or conventional lacquer additives, together with at least one of the following modules:

15 B) one or more colour modules containing water, one or more coloured pigments and/or extenders and one or more cationically stabilised polyurethane paste resins, at least 6 wt.% of water, optionally together with one or more water-dilutable cationically and optionally non-ionically stabilised binders, one or more organic solvents and/or conventional lacquer additives, and/or

20 C) one or more effect modules containing water, one or more effect pigments, at least 6 wt.% of water, one or more cationically stabilised water-dilutable (meth)acrylated polyurethane resins, which may optionally be present combined with further cationically or non-ionically stabilised water-dilutable binders, optionally together with one or more organic solvents and/or conventional lacquer additives and/or

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D) one or more crosslinking modules containing one or more crosslinking agents, optionally together with one or more organic solvents, water and/or conventional lacquer additives, and/or

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E) one or more rheological modules containing one or more organic and/or inorganic rheological control agents, optionally together with one or more cationically, or cationically and non-ionically and/or non-ionically stabilised water-dilutable binders and/or one or more organic solvents and/or water.

2. Process for the production of aqueous coating compositions by mixing at least one aqueous binder component with further coating composition components, characterised in that a supply of at least one storage-stable binder module A) according to claim 1, optionally together with at least one storage-stable module each of B), C), D) and/or E) according to claim 1, is prepared and optionally stored, the modules being separately prepared, and the individual prepared modules are mixed together as required in quantities such that the solids content arising therefrom, relative to the total solids content of the coating compositions, assumes the following percentages:

binder modules A): 5 - 99 wt.%

colour modules B): 0 - 60 wt.%

30 effect modules C): 0 - 50 wt.%

crosslinking modules D): 0 - 50 wt.%

rheological modules E): 0 - 50 wt.%

35 wherein the sum of the percentages should amount to 100%.

3. Modular system and process according to claim 1 or 2, characterised in that the binder module A) contains 10-99 wt.% of the cationically stabilised (meth)acrylic copolymer, 2-70 wt.% of the cationically stabilised polyurethane resin and 0.2-60 wt.% of the cationically stabilised (meth)acrylated polyurethane resin, wherein the stated percentages relate to the total binder solids content in the binder module and should add up to 100%.

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4. Modular system and process according to one of the preceding claims, characterised in that the colour modules B) and effect modules C) each contain at least 10 wt.% of water.

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5. Modular system and process according to one of the preceding claims, characterised in that one or more cationically stabilised (meth)acrylic copolymers with an OH value of 30 to 200, a number average molecular weight (M_n) of 1000 to 200000 and an amine value of 15 to 150 are used.

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6. Modular system and process according to one of claims 1 to 4, characterised in that one or more cationically stabilised polyurethane resins with a number average molecular weight (M_n) of 3000 to 200000 and an amine value of 15 to 120 are used.

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7. Modular system and process according to one of claims 1 to 4, characterised in that one or more cationically stabilised (meth)acrylated polyurethane resins with an amine value of 5 to 150 and an OH value of 0 to 150 are used.

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8. Modular system and process according to one of the preceding claims, characterised in that the binder modules have a pH value of 5 to 7.
- 5 9. Modular system and process according to one of the preceding claims, characterised in that the crosslinking modules contain one or more melamine resins and/or blocked or unblocked polyisocyanates.
- 10 10. Modular system and process according to one of the preceding claims, characterised in that the rheological modules contain polymer microparticles, inorganic phyllosilicates and/or associative thickeners.
- 15 11. Modular system and process according to claim 10, characterised in that the associative thickeners used are one or more cationic associative thickeners based on polyurethane resins with hydrophilic segments in the main chain and hydrophobic segments on the chain ends, with an amine value of 5 to 100 and an OH value of 0 to 70.
- 20 12. Process according to one of the preceding claims, characterised in that the total solids content of the coating composition is adjusted to 10 to 80 wt.% at application viscosity.
- 25 13. Process according to claim 12, characterised in that aqueous effect base lacquers, single-tone aqueous base lacquers, aqueous single-coat topcoat lacquers and/or aqueous clear lacquers are produced using the same binder modules.
- 30 35 14. Process according to claim 2, 12 or 13, characterised in that an aqueous effect base lacquer is produced

with a proportion, in accordance with the solids content defined in claim 2, of:
binder module of 10 to 99 wt.%,
colour module of 0 to 40 wt.%,
5 effect module of 0.01 to 50 wt.%
crosslinking module of 0 to 40 wt.%,
rheological module of 0.01 to 50 wt.%,
wherein the solids content of the coating composition
is adjusted to 10 to 55 wt.% at application viscosity.

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15. Process according to claim 2, 12 or 13, characterised in that a single-tone aqueous base lacquer is produced with a proportion, in accordance with the solids content defined in claim 2, of:
binder module of 5 to 60 wt.%,
colour module of 1 to 60 wt.%,
crosslinking module of 0 to 40 wt.%,
rheological module of 0 to 40 wt.%,
wherein the solids content of the coating composition
20 is adjusted to 10 to 60 wt.% at application viscosity.

16. Process according to claim 2, 12 or 13, characterised in that an aqueous single-coat topcoat lacquer is produced with a proportion, in accordance with the
25 solids content defined in claim 2, of:
binder module of 5 to 60 wt.%,
colour module of 0.5 to 60 wt.%,
effect module of 0 to 50 wt.%,
crosslinking module of 0.5 to 40 wt.%,
30 rheological module of 0 to 40 wt.%,
wherein the solids content of the coating composition
is adjusted to 10 to 70 wt.% at application viscosity.

35 17. Process according to claim 2, 12 or 13, characterised in that an aqueous clear lacquer is produced with a proportion, in accordance with the solids content defined in claim 2, of:

binder module of 15 to 90 wt.%,
colour module of 0 to 20 wt.%,
effect module of 0 to 10 wt.%,
crosslinking module of 0.01 to 50 wt.%,
5 rheological module of 0 to 40 wt.%,
wherein the solids content of the coating composition
is adjusted to 10 to 80 wt.% at application viscosity.

18. Aqueous coating compositions produced using the
10 process of one of claims 2 to 17.

Abstract:

Modular system for the production of aqueous coating compositions, containing

- A) at least one aqueous binder module containing one or more cationically stabilised water-dilutable (meth)acrylic copolymers and cationically stabilised water-dilutable polyurethane resins and/or cationically stabilised water-dilutable (meth)acrylated polyurethane resins, optionally combined with non-ionically stabilised water-dilutable binders, water, optionally together with organic solvents and/or conventional lacquer additives, together with at least one of the following modules:
- B) one or more colour modules containing water, coloured pigments and/or extenders and cationically stabilised paste resins, at least 6 wt.% of water, optionally together with water-dilutable cationically and optionally non-ionically stabilised binders, organic solvents and/or conventional lacquer additives, and/or
- C) one or more effect modules containing water, effect pigments, at least 6 wt.% of water, cationically stabilised water-dilutable (meth)acrylated polyurethane resins, which may optionally be present combined with further cationically or non-ionically stabilised water-dilutable binders, optionally together with organic solvents and/or conventional lacquer additives and/or

- D) one or more crosslinking modules containing one or more crosslinking agents, optionally together with organic solvents, water and/or conventional lacquer additives,
and/or
- E) one or more rheological modules containing one or more organic and/or inorganic rheological control agents, optionally together with cationically, or cationically and non-ionically and/or non-ionically stabilised water-dilutable binders and/or organic solvents and/or water.